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COATINGS

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GLASS CERAMIC ELECTRIC INSULATION COATINGS FOR THICK-FILM ENERGY-SATURATED SYSTEMS

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Glass-ceramic electrical insulation ceramic coatings with working temperatures to 400°C for stainless-steel substrates were developed. Their physical-chemical properties were studied.

Key words: electrical insulation coating, frit, synthesis, electric conductivity, chemical stability.

The development of competitive products which are cost-competitive in the radio-electronics market has led to the appearance of a modern, thick-film technology for obtaining metal-dielectric substrates and pastes with no precious metals. The aim of this technology is to lower significantly the cost of maintaining or increasing the quality and reliability of powerful hybrid integrated circuits and domestic heating equipment.

Electrical insulation coatings used for forming dielectric layers of thick-film capacitors, interlayer insulation, as sealing coatings for semiconductor devices and for developing multilayer switching occupy a special place among the materials of thick-film technology. They also find applications in household appliances as insulation layers in heaters for flat-irons, rings for cooking stoves, drying cabinets and other articles.

Considering the numerous theoretical and experimental research performed using the composition – property scheme, in the present work special attention was devoted to studying the regularities of coating formation on metallic substrates, the effect of the structural state of properties specific to electrical insulation glass and the nature of their interaction during formation.

The results of research on these processes open up the possibility of controlling the properties of coatings by purposeful selection of the glass composition and controllable conditions for coating formation [1 – 3].

An important problem is to develop high-quality electrical insulation coatings for the aviation and electronics industries.

The complexity of this work lay in the obtaining a comprehensive solution to the problem of synthesizing a high-quality dielectric. It was necessary on the one hand to optimize the physical-chemical properties of glass and on the other to study the processes occurring during the formation of dielectric layers on a metal in order to determine the general rules of the interaction.

Analysis of the published data shows that barium-containing aluminum-borate glasses could be of greatest interest, since they possess the highest electrical resistance and quite high linear thermal expansion coefficient (CLTE) [4].

Considering the enormous experience gained in using electrical insulation glasses and protective technological coatings in industry, glasses in the aluminum borosilicate system, especially with alkali-free compositions containing oxides of alkaline-earth metals, are of greatest interest for finding and developing glassy dielectrics [5, 6].

An advantage of alkali-free aluminum borosilicate systems are high electrical insulation characteristics and high chemical and thermal stability. Introducing oxides of alkaline-earth metals into such glasses makes it possible to improve the glassmaking and technological properties and increase the CLTE.

The introduction of B_2O_3 into a silicon-oxygen framework decreases and, conversely, Al_2O_3 increases the conductivity of glass. It is presumed that the effect of B_2O_3 and Al_2O_3 on the conductivity is due to the degree of ordering of the distribution of impurities in the glass matrix. It should

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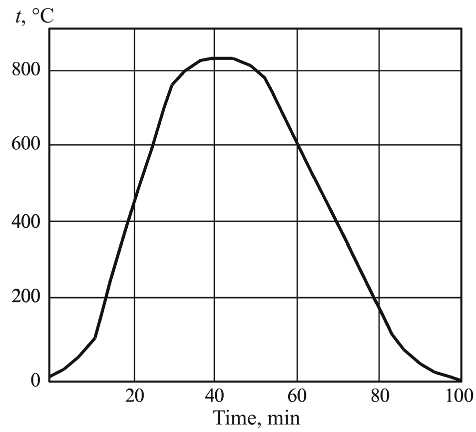

Fig. 1. Temperature – time diagram of the formation of a dielectric insulation coating.

also be noted that glass enriched with boron oxide decompose into phases, one of which is represented by a tetrahedral aluminum-silicon-oxygen network and the other by a boron-oxygen network, including boron in three- and four-fold coordination.

The large differences in the lengths of the bonds B–O (1.48 Å) and Si–O (1.6 – 1.63 Å) make BO_4 and SiO_4 tetrahedra structurally incompatible, which is why glasses containing BO_4 and SiO_4 tetrahedral groups are immiscible.

Divalent metal oxides are widely used to improve the physical and chemical properties of alkali-free aluminum-borosilicate glasses. Analysis of the literature shows that barium-containing aluminum-borate glasses are of greatest interest for synthesis of electrical insulation coatings, since such glass possesses the highest electrical resistance and CLTE (with the exception of lead-containing glass).

The BaO content by weight must be no lower than 20% in order to obtain quite high CLTE. On the basis of the positions of the immiscibility regions in the system SiO_4–BaO–B_2O_3 in glasses containing up to 20% BaO the maximum amount of B_2O_3 cannot exceed 15%, otherwise the glasses become highly prone to separation into layers.

The following research directions were picked in the present worked:

– picking an experimental procedure;

– developing compositions for electrical insulation coatings in the system Al_2O_3–BaO–B_2O_3;

– studying the physical, chemical and electrical properties of coatings.

Significant attention was devoted to studying the electrical properties of coatings, specifically, the electrical resistance and the breakdown voltage. Together with the properties indicated above, measurements were made of the CLTE, deformation onset temperature $T_{d.o}$ and flowability of the coatings.

An M4100/400 mega-ohmmeter with heating to 600°C was used to study the dielectric properties of the coatings.

TABLE 1. Physical and Chemical Properties of Frit No. 8

System	Density, g/cm^3	CLTE, 10^{-8} K^{-1}	$T_{d.o}$, °C	Viscosity P, at 900 – 1020°C
SiO_2–BaO–CaO	3.5	8.3	780	$10^9 – 10^5$

The samples for the tests consisted of 40 × 60 × 3 mm rectangular metallic plates made of the alloy KH18N10T. An enamel coating protected the surfaces of the plates.

The initial materials and finished coatings were investigated by standard procedures used to determine the physical and chemical properties of glasses. Silicate frit (No. 8), synthesized in the system SiO_2–BaO–B_2O_3 with high BaO content, was used to synthesize the coatings.

The coatings obtained using the synthesized frits were prepared following the adopted enameling technology by grinding them for 40 h in porcelain drums using alundum balls with water added. The coatings were deposited in two or three layers from a paint sprayer with slip viscosity 18 – 19 sec (VZ-246 viscosimeter). The coating was fired at temperature 800 – 830°C, the soaking time was 3 – 5 min and the protective dielectric layer was 120 – 150 μm thick (Fig. 1).

The physical and chemical properties of No. 8 frit are presented in Table 1.

A drawback of the coatings prepared using No. 8 frit is high formation temperature. At coating formation temperatures 900 – 1000°C the metallic base is subject to buckling. An effective method of lowering the coating formation temperature is to change the composition of the coating by introducing low-melting components, e.g., boron oxide, into the coating composition.

Boron oxide was added to No. 8 frit during melting of the experimental compositions (10 – 40 wt.% B_2O_3, 60 – 90 wt.% frit).

The following modifying additives were used to improve the technological characteristics: ZnO, Fe_2O_3 and Co_2O_3. The main purpose of the modifying additives is to decrease the refractoriness and improve the physical and chemical properties (flowability, bonding strength with a metallic substrate) of the coating.

Dry slips were used to investigate the physical and chemical properties of the coatings. The slips were used to fabricate samples for determining the fusibility, CLTE and flowability.

The results showed that as B_2O_3 is added to the glass composition the softening onset temperature decreases gradually from 780 to 700°C (Fig. 2).

It was determined that the softening onset temperature decreases by 25°C when 3 – 5 wt.% ZnO is added to the frit. Increasing ZnO above this amount does not greatly change the softening temperature range.

As the B_2O_3 content increases in No. 8 frit coating flow improves and the contact angle θρ° of flow is 36°. Better re-

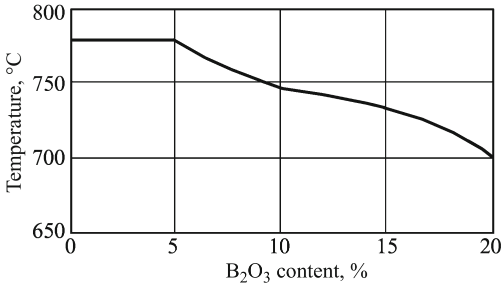

Fig. 2. Effect of B_2O_3 content on the softening onset temperature $t_{s.o}$ of the coating.

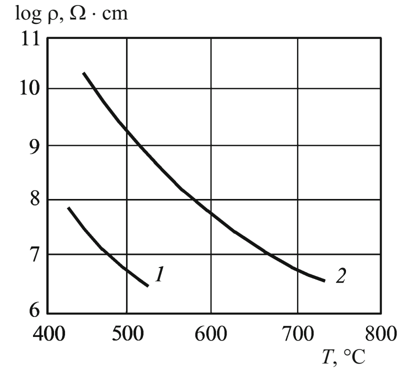

Fig. 3. Effect of temperature on the electrical resistance of the coatings: *1*) known compositions ÉV-300-60M and ÉVK-103; *2*) synthesized compositions.

sults for coating flow were obtained by introducing Fe_2O_3 and ZnO.

Increasing the B_2O_3 content in No. 8 frit decreases the CLTE considerably from 8.6×10^{-6} K^{-1} to 6.7×10^{-6} K^{-1}.

The chemical stability of the synthesized frits was determined by a simplified method.

The mass losses were determined by weighing dried samples of powder before and after soaking in a water bath.

According to the determination of the relative mass losses of the samples of technological specimens of the frit powder and the classification of the hydrolytic classes of instrument glass the powder is a class 2 stable glass.

A qualitative assessment was made of frit leaching during heating in distilled water on a water bath by determining the pH of the solution. The measurements were performed with a pH-673.H apparatus. Frit leaching was not observed; the pH of the solution of specimens before and after heating was 8.2 ± 0.20.

The TK-100 temperature, at which the resistivity $\rho = 10^8$ Ω, was adopted as a measure of the temperature stability of the dielectrics.

The effect of the heating temperature on the electrical resistance of the coatings was investigated. The resistance was recorded using a M4100/400 mega-ohmmeter at the voltage potential 1000 V. The frits were heated to 650°C. To compare the effectiveness of the synthesized frits the electrical resistance of the well-known coatings ÉV-300-60M and ÉVK-103 was measured. The values of the electrical resistance as well as the TK-100 value graphically reflect the advantages of the experimental frits (Fig. 3). For the synthesized coatings TK-100 lies in the range 450 – 500°C, while for the coating ÉV-300-60M the decrease of the electrical resistance is observed even at lower temperatures (TK-100 = 290°C). The data obtained reflect the effect of the chemical composition of the glass on the electrical resistance. It is known that the increase in the electrical resistance of the synthesized frit compositions is due to the high insulation properties of the main component of the coating (boron oxide) and the compact packing of its structural elements BO_3 (BO_4) in the spatial network.

The electrical strength of the frits was determined by their capability of withstanding high electric fields without breakdown or insulation losses. The present investigations showed that the experimental composition can withstand voltages to 3000 V.

Service life tests of the samples with synthesized optimal properties and total operating time 300 h were conducted at temperatures 200°C and 300°C (100 h). The samples were heat-treated in the regimes indicated, after which they were tested for electrical strength at voltage 1000 V and the electrical resistance was measured. It was found that the dielectric layer does not break down at high voltages; therefore, the electrical resistance remains close to the initial value ($\rho = 10^{16}$ Ω).

The thermal stability tests of the samples were conducted at 200 – 400°C, τ = 300 h, with 15-fold cooling to room temperature in different time intervals. The data obtained showed that after the tests the continuity of the enamel layer was undisturbed and no other defects, such as chips or pits, were observed.

On the basis of the theoretical studies and experimental data a concept was developed for synthesis and methodological approaches to producing electrical insulation coatings consisting of a thermodynamically stable framework (matrix) and complex fill were found.

Oxide-modified glasses in the aluminum-borosilicate system Al_2O_3–B_2O_3–SiO_2 were studied.

The synthesized alkali-free compositions have the following advantages of high dielectric characteristics and chemical and thermal stability. The technological properties can be improved and the CLTE increased by adding alkaline-earth metals into glass in the indicated system.

A comprehensive investigation of the synthesis, formation and temperature interaction in the systems coating – steel – medium made it possible to develop electrical insulation glass-ceramic coatings with working temperatures to 400°C for stainless steel substrates.

Electrical insulation coatings make it possible to replace ceramic substrates with metal-dielectric substrates for hybrid integrated circuits and increase the life and thermal stability of articles.

REFERENCES

1. S. S. Solntsev, *Protective Technological Coatings and Refractory Enamels* [in Russian], Mashinostroenie, Moscow (1984).
2. S. S. Solntsev, V. A, Rozenenkova, N. V. Isaeva, and V. V. Shvagereva, "Application of glass ceramic materials and coatings in aerospace technology," in: *Anniversary Collection of Scientific and Technical Works* [in Russian], VIAM, Moscow (2002), pp. 137 – 150.
3. S. S. Solntsev, "High-temperature composite materials and coatings based on glass and ceramic," in: *Anniversary Collection of Scientific and Technical Works* [in Russian], VIAM, Moscow (2002), pp. 90 – 99.
4. A. A. Appen, *Glass Chemistry* [in Russian], Khimiya, Leningrad (1974).
5. N. I. Nefedov and L. V. Semenova, "Trends in conformal coatings for moisture protection and electrical insulation of printed boards and elements of radioelectronic apparatus," *Aviats. Mater. Tekhnol.*, No. 1, 8 – 12 (2013).
6. A. V. Panarin, "Pyrolytic chromium carbide coatings: fabrication technology and properties," *Aviats. Mater. Tekhnol.*, No. 4, 12 – 15 (2011).